CLEANI NG METHOD OF FI LTER MEMBRANE MODULE

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Inventor(s): NAKATSUKA NOBUYUKI
Applicant(s): DAICEL CHEM
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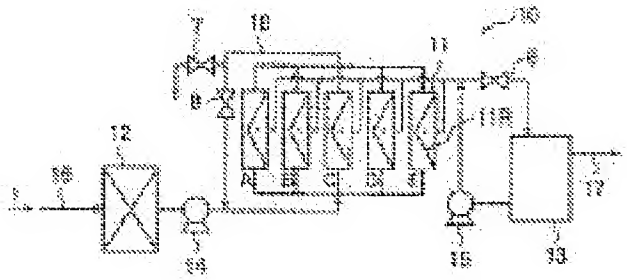
Abstract of **JP 11076769 (A)**

PROBLEM TO BE SOLVED: To obtain a cleaning method of a filter membrane module capable of sufficiently removing an adsorbed material to the filter membrane, improving cleaning effect, reducing the consumption of a liquid chemical, cleaning with the liquid chemical for a short time and decreasing cleaning cost in a liquid chemical cleaning process of the filter membrane. SOLUTION: In the cleaning method of the filter membrane module 11 for recovering the water permeability by cleaning the filter membrane module 11 degraded in water permeability of a membrane purifying system 10 of water with the liquid chemical, at least one point of time before and after the liquid chemical is supplied to the filter membrane module 11 or at the both point of time, a gas pressurizing process for pressurizing a gas from the permeation side of the filter membrane of the filter membrane module 1 at >=20 kPa to below the bubble point is provided for 1-5 min.



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(71)出願人　000002901
ダイセル化学工業株式会社
大阪府堺市鉄砲町１番地

(72)発明者　中塚　修志
兵庫県姫路市網干区新在家1239番地　ダイセル化学工業株式会社総合研究所内

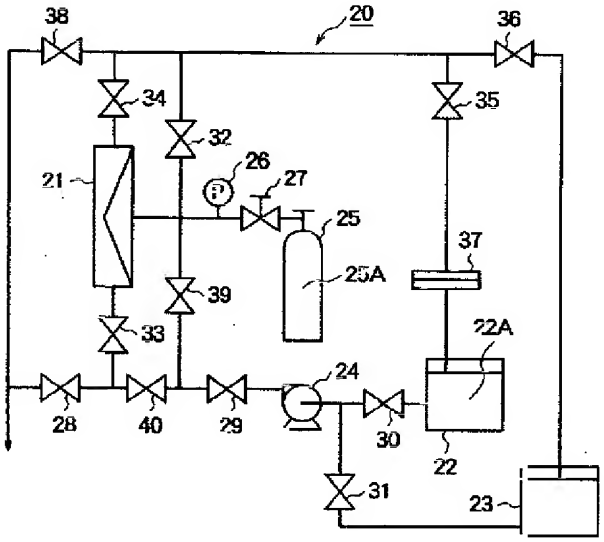
(74)代理人　弁理士　三浦　良和

(54)【発明の名称】　濾過膜モジュールの洗浄方法

(57)【要約】

【課題】　沪過膜の薬液洗浄工程において、沪過膜への吸着物質の十分な除去ができ、洗浄効果を向上でき、かつ薬液の使用量を減らすとともに、短時間で薬液洗浄が行え、さらに、洗浄コストを下げることのできる沪過膜モジュールの洗浄方法を得ることを目的とする。

【解決手段】　水の膜浄化システムの透水性能が低下した沪過膜モジュールを、薬液によって洗浄して透水性能を回復させる沪過膜モジュールの洗浄方法において、薬液を沪過膜モジュールに供給する前あるいは後のいずれか一方またはその両方の時点で、気体を沪過膜モジュールの沪過膜の透過側から圧力２０ｋＰａ以上バブルポイント未満で加圧する気体加圧工程を０．１～５分間設けることを特徴とするものである。



【特許請求の範囲】
【請求項１】水の膜浄化システムの透水性能が低下した沪過膜モジュールを薬液によって洗浄して透水性能を回復させる沪過膜モジュールの洗浄方法において、　薬液を沪過膜モジュールに供給する前あるいは後のいずれか一方またはその両方の時点で、気体を沪過膜モジュールの沪過膜の透過側から圧力２０ｋＰａ以上バブルポイント未満で加圧する気体加圧工程を０．１～５分間設けることを特徴とする沪過膜モジュールの洗浄方法。
【請求項２】水が、表流水であることを特徴とする請求項１に記載の沪過膜モジュールの洗浄方法。
【請求項３】沪過膜が、限外沪過膜であることを特徴とする請求項１または２に記載の沪過膜モジュールの洗浄方法。
【請求項４】沪過膜モジュールが、中空糸膜からなる中空糸膜モジュールであることを特徴とする請求項１～３のいずれか１項に記載の沪過膜モジュールの洗浄方法。
【請求項５】沪過膜の膜材質が、酢酸セルロースであることを特徴とする請求項１～４のいずれか１項に記載の沪過膜モジュールの洗浄方法。
【請求項６】薬液による洗浄が、クエン酸、界面活性剤及び次亜塩素酸ナトリウムのうちから選択される一種もしくは二種以上の組み合わせまたは１段もしくは多段に組み合わて行うことを特徴とする請求項１～５のいずれか１項に記載の沪過膜モジュールの洗浄方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、沪過膜モジュールの洗浄方法に関し、特に、沪過膜モジュールを薬液により洗浄して透水性能を回復させる場合、短時間の洗浄で透水性能を回復させ、洗浄後も長期にわたり安定運転を可能とする沪過膜モジュールの洗浄方法に関する。
【０００２】
【従来の技術及び発明が解決しようとする課題】従来、透水性能が低下した沪過膜モジュールを薬液で洗浄する方法として、例えば、透過液室の圧力と原液室の圧力を等しくした状態で薬液を循環させる沪過膜モジュールの洗浄方法が特開昭６１－１１１０８号公報に開示されている。また、特開平３－７７６２９号公報や特開平４－１６１２３２号公報には、透過側から薬液を加圧注入する沪過膜モジュールの洗浄方法が開示されている。しかしながら、薬液のみの単独の洗浄方法では十分な洗浄効果が得られないという問題点がある。洗浄効果が不十分な場合、従来の方法では薬液の使用量を増したり、薬洗時間を延ばして洗浄効果を上げる方法がとられている。
【０００３】また、透過側から気体を圧入する沪過膜モジュールの洗浄方法としては、例えば、専門誌　”膜” Vol.20 No.5, p328(1995)に開示されている。これは、透過側から圧入された気体が沪過膜を瞬時に通過して目詰まり物質を取り除き、沪過流束を維持する逆洗方法である。しかしながら、この気体の圧入が薬液洗浄工程における洗浄方法ではないため、酸化鉄や酸化マンガンなどの沪過膜への吸着物質は除去することができないという問題点がある。
【０００４】そこで、本発明は、沪過膜の薬液洗浄工程において、沪過膜への吸着物質の十分な除去ができ、洗浄効果を向上でき、かつ薬液の使用量を減らすとともに、短時間で薬液洗浄が行え、さらに、洗浄コストを下げることのできる沪過膜モジュールの洗浄方法を提供することを目的とする。
【０００５】
【課題を解決するための手段】本発明者らは、沪過膜モジュールの薬液洗浄工程の洗浄方法において、薬液の沪過膜モジュールへの供給と気体の沪過膜への加圧のタイミング等につき種々検討の結果、その加圧のタイミング及び気体の加圧による洗浄効果に大きな差異を見いだし、且つ、沪過膜の種類、薬液の組み合わせ、薬液洗浄の順序回数等につき種々検討の結果、短時間に優れた洗浄効果が得られることを見いだし、本発明を完成するに至った。
【０００６】すなわち、本発明の沪過膜モジュールの洗浄方法は、水の膜浄化システムの透水性能が低下した沪過膜モジュールを薬液によって洗浄して透水性能を回復させる沪過膜モジュールの洗浄方法において、　薬液を沪過膜モジュールに供給する前あるいは後のいずれか一方またはその両方の時点で、気体を沪過膜モジュールの沪過膜の透過側から圧力２０ｋＰａ以上バブルポイント未満で加圧する気体加圧工程を０．１～５分間設けることを特徴とするものである。
【０００７】また、本発明の沪過膜モジュールの洗浄方法は、水が、表流水であることを特徴とするものである。
【０００８】また、本発明の沪過膜モジュールの洗浄方法は、沪過膜が、限外沪過膜であることを特徴とするものである。
【０００９】また、本発明の沪過膜モジュールの洗浄方法は、沪過膜モジュールが、中空糸膜からなる中空糸膜モジュールであることを特徴とするものである。
【００１０】また、本発明の沪過膜モジュールの洗浄方法は、沪過膜の膜材質が、酢酸セルロースであることを特徴とするものである。
【００１１】また、本発明の沪過膜モジュールの洗浄方法は、薬液による洗浄（薬液洗浄とも略す）が、クエン酸、界面活性剤及び次亜塩素酸ナトリウムのうちから選択される一種もしくは二種の組み合わせまたは１段もしくは多段に組み合わて行うことを特徴とするものである。
【００１２】
【発明の実施の形態】本発明において、気体の加圧は薬液を沪過膜モジュールに供給する前あるいは後のいずれ

か一方またはその両方の時点で行ってよいが、薬液を供給する前あるいは両方が好ましい。沪過膜面に付着した目詰まり物質を予め物理的に除去し、その後の薬液による洗浄効果を上げる理由から、薬液を沪過膜モジュールに供給する前が最も好ましい。本発明の沪過膜モジュールの洗浄方法において、気体を沪過膜モジュールの沪過膜の透過側から導入する圧力は、２０ｋＰａ以上バブルポイント未満であり、好ましくは４０ｋＰａ以上１５０ｋＰａ以下である。ここに、気体の圧力を２０ｋＰａ以上バブルポイント未満としたのは、圧力が２０ｋＰａより低いと洗浄効果が不十分であり、目的とする洗浄回復性が得られず、また、圧力がバブルポイント以上では沪過膜モジュールに物理的ダメージを与えてしまうからである。ここに、バブルポイントは沪過膜の材質、沪過膜の分画分子量または膜孔径にもよるが、例えば膜孔径０．１μｍの酢酸セルロース膜では約３００ｋＰａである。

【００１３】また、気体加圧工程では、気体を膜の透過側に導入する際、気体は沪過膜を透過し原水側に押し出される必要はなく、気体が沪過膜の透過側から膜厚内部に圧入されていればよい。このような気体による圧入を行うと、気体が沪過膜モジュール内の沪過膜全体の膜厚内部に侵入し、汚染した沪過膜の目詰まり物質を押し出すため、沪過膜モジュール内部が均一に洗浄できるという特長があるからである。通常の逆洗のように液体（薬液）を沪過膜モジュールの透過側から加圧すると、液体が膜面の比較的に目詰まりのない部分を透過してしまい、目詰まり部分を透過しにくいため、目詰まり部分を洗浄することができず、沪過膜の不均一な洗浄となる。

【００１４】また、気体の加圧時間（気体加圧工程）は、気体が沪過膜モジュール内の沪過膜の全ての透過側に実質的に加圧されている時間であり、０．１～５分間が望ましいが、洗浄効果と効率を考慮すると、好ましくは０．５～２分間である。ここに気体の加圧時間を０．５～５分間としたのは、０．５分未満では気体が目詰まり部分に十分に行きわたらず、目詰まり部分の洗浄の効果が十分ではない、また、５分を超えると洗浄の効果の向上は少なく、洗浄効率が低下するからである。

【００１５】本発明の沪過膜モジュールの沪過膜は、特に限定されないが、精密沪過膜、限外沪過膜、ナノ沪過膜及び逆浸透膜などがある。精密沪過膜では、気体を透過側から加圧すると、気体が沪過膜を通過してしまう場合があるため、均一な洗浄が困難となる。また、ナノ沪過膜や逆浸透膜では、沪過膜の膜孔径が小さすぎて気体が沪過膜の孔内部に侵入できない場合があり、十分な洗浄効果が得られなくなる。従って、本発明の沪過膜としては、限外沪過膜が好ましい。ここで限外沪過膜とは、分画分子量が10^3～10^6であり、膜孔径が１～１００ｎｍの沪過膜をいう。

【００１６】本発明の沪過膜モジュールの膜材質としては、ポリエーテルスルホン、ポリアクリロニトリル共重合体及び酢酸セルロースなどの高分子があるが、酢酸セルロースが特に好ましい。

【００１７】本発明の沪過膜モジュールの膜形態としては、プレート・アンド・フレーム型、プリーツ型、スパイラル型、チューブラー（管状）型及び中空糸型があるが、中空糸型が好ましい。また、中空糸膜モジュールを用いる場合には、中空糸膜の内側に原水を流入させる内圧方式が好ましい。

【００１８】本発明において、薬液洗浄を一種もしくは二種以上の組み合わせて行う例として、クエン酸と界面活性剤を組み合わせた「組み合わせ薬液」を用いることを挙げることができる。また１段または多段に組み合わせるとは、１段の場合は上記の薬液による洗浄を一度だけ行うことを意味し、多段の場合は薬液による洗浄を数回行うことを意味する。クエン酸と界面活性剤を用いて沪過膜モジュールを多段で洗浄する場合の形態としては、①クエン酸で洗浄し、つぎに界面活性剤で洗浄する例、②両者の組み合わせ薬液で数回洗浄する例、など種々の組み合わせがある。これらの洗浄の間または前後に気体加圧工程を適宜入れてもよいのは勿論である。薬液洗浄時の薬液は、沪過膜の原水側を循環させてもよいし、原水側から透過側に循環させてもよい。さらに、沪過膜の透過側から原水側に流すようにしてもよい。

【００１９】

【実施例】以下、本発明の実施例を図面に基づき説明するが、本発明は、以下の実施例に限定されるものではない。図１は本発明の沪過膜モジュールの洗浄方法を実施するための沪過膜モジュール１１Ａ～Ｅを用いた膜浄化システムである沪過運転装置１０の概略図であり、流量計や圧力計などの付属設備は省略している。図１において、１１は沪過膜モジュールであり、５本の組み合わせで、それぞれ沪過膜モジュール１１Ａ、１１Ｂ、１１Ｃ、１１Ｄ、１１Ｅ（代表として１１で示す）とする。沪過膜モジュール１１は、沪過膜１１Ｒの膜材質が酢酸セルロースで、中空糸膜からなる中空糸膜モジュールを表したものであり、各中空糸膜モジュールは内径０．８ｍｍ、外径１．３ｍｍの中空糸からなり、一つのモジュールの膜面積は０．５m^2である。１２はプレフィルターであり、プレフィルター１２は沪過膜モジュール１１に供給する水である表流水中の異物を除去する。１３は透過水タンクであり、透過水タンク１３は沪過膜モジュール１１からの透過水を一時貯蔵する。１４、１５はポンプである。６、７、８は、開閉弁である。

【００２０】沪過運転時には、開閉弁７は閉じ、開閉弁６、８は開いている。表流水である河川原水１は、取水パイプ１６から供給され、プレフィルター１２で異物が除去され、ポンプ１４で５本の沪過膜モジュール１１Ａ～１１Ｅのそれぞれに供給される。沪過膜モジュール１１では、河川原水は中空糸沪過膜１１Ｒの内側に供給さ

れ、内圧クロスフロー沪過された透過水は開閉弁６を通って集水され、透過水タンク１３に一時貯蔵され、浄化水としてパイプ１７から送り出される。沪過されなかった原水は循環パイプ１８を介して開閉弁８を通り、循環するようになされている。沪過膜モジュール１１の沪過は、クロスフロー線速０．２ｍ／ｓで、設定沪過流束１．５ｍ／日の定流量沪過である。また、運転は、４５分おきに１回の割合で、透過水を沪過膜モジュールの透過側から１分間流す逆洗工程を設け、水回収率を９０％とされている。逆洗運転時には、開閉弁７は開き、開閉弁６、８は閉じ、ポンプ１４は停止している。そして透過水の一部をポンプ１５を介して通常運転とは逆向きに沪過膜モジュール１１の透過側に供給する逆洗を定期的に実施できる様になっている。

【００２１】（実施例１）図２は本発明の実施例１を示す図であり、２０は本発明の沪過膜モジュールの洗浄方法を実施するための沪過膜モジュールの薬液洗浄装置である。まず、図２に示す薬液洗浄装置２０の構成につき説明する。２１は沪過膜モジュール、２２は沪過膜モジュールを薬液洗浄するための薬液２２Ａを貯蔵した薬液槽、２３は純水を貯蔵した純水槽、２４はポンプ、２５は気体である圧縮空気２５Ａを貯蔵した空気圧ボンベ、２６は圧力ゲージ、２７は圧力調節弁、２８、２９、３０、３１、３２、３３、３４、３５、３６、３８、３９および４０は開閉弁、３７はフィルターである。薬液洗浄装置２０において、開閉弁３２および３９を閉じた状態で、空気圧ボンベ２５のバルブを開き、圧力調節弁２７を調節することにより、空気２５Ａを沪過膜モジュール２１の透過側に所定の圧力で圧入できるようになされている。また、開閉弁２９、３０、３３、３４、３５および４０を開、開閉弁２８、３１、３２、３６、３８および３９を閉として、ポンプ２４を駆動させることにより、薬液槽２２内の薬液２２Ａを循環させて、沪過膜モジュール２１を薬液洗浄することが可能である。循環洗浄後、さらに開閉弁２８を開として、薬液２２Ａを排出した後、開閉弁３１、２９、３３、３４、３６、３２および４０を開に、開閉弁３０、２８、３５、３８および３９を閉にしてポンプ２４を稼働させて、回復率を求めるための純水透過流束を測定できるようになされている。

【００２２】本実施例では、まず、図１における沪過運転装置１０において、沪過膜モジュール１１に、純水透過流束が８．４ｍ／日の純水透水能力を有する沪過膜モジュール１１Ａ～Ｅの５本を取り付けた。そして、河川下流の河川原水（表流水）１を沪過運転装置の取水パイプ１６から取水し、沪過運転を開始した。沪過運転は、中空糸膜の内側に原水を供給する内圧クロスフロー沪過（クロスフロー線速０．２ｍ／ｓ）であり、設定沪過流束１．５ｍ／日の定流量沪過で実施した。また、運転は、４５分おきに１回、透過水を沪過膜モジュールの透過側から１分間流す逆洗工程を設け、水回収率を９０％とした。この定流量沪過運転では、沪過膜が原水中の異物により汚れ、目詰まりするとともに、沪過圧力が徐々に増加し、運転開始から約８ヶ月後に５本の沪過膜モジュールがともに沪過圧力が１００ｋＰａに達して運転の継続が行えなくなった。これらの５本の沪過膜モジュール１１Ａ～１１Ｅを沪過運転装置１０から取り外し、図２に示す薬液洗浄装置２０の沪過膜モジュール２１に代えて順に取り付け、沪過膜モジュール１１に純水を１００ｋＰａ加圧で透過し、純水透過流束を測定したところ、いずれも１．３～１．８ｍ／日であり、運転前の純水透過流束８．４ｍ／日から著しく透水性能が低下した。

【００２３】次いで、上記運転後の沪過膜モジュール１１の洗浄を行った。先ず、運転後の沪過膜モジュール１１Ａ（純水透過流束１．５ｍ／日）を、図２に示す薬液洗浄装置２０の沪過膜モジュール２１の代わりに取り付け、開閉弁３２および３９を閉の状態で空気圧ボンベ２５から圧力調節弁２７によって空気圧５０ｋＰａに調節した空気２５Ａを沪過膜モジュール２１の透過側に１分間圧入した。すなわち、気体加圧工程を設けた。次いで、薬液洗浄のため、開閉弁２９、３０、３３、３４、３５および４０を開、開閉弁２８、３１、３２、３６、３８および３９を閉として、ポンプ２４を駆動させて、薬液タンク２４中のクエン酸水溶液（１ｗｔ％）を膜面での平均線速が０．５ｍ／ｓとなるように３０分間循環させて、沪過膜モジュールを薬液洗浄した後、開閉弁２８を開とし、薬液を排出した。その後、前記と同様にして、沪過膜モジュール１１Ａの純水透過流束を測定したところ、８．３ｍ／日であり、ほぼ運転前の透過流束にまで回復するという優れた洗浄効果を得ることができた。

【００２４】（実施例２）実施例２においては、実施例１における沪過運転装置１０を用い、定流量沪過運転により透水性能が低下した沪過膜モジュール１１Ｂ（純水透過流束１．８ｍ／日）を、図２に示す薬液洗浄装置２０の沪過膜モジュール２１の代わりに取り付けた。そして沪過膜モジュール１１Ｂの透過側に空気を圧入する前に、クエン酸水溶液（１ｗｔ％）を１０分間循環させて洗浄した後、透過側に１００ｋＰａの空気２５Ａを圧入して、沪過膜モジュール１１Ｂの透過側を１分間空気２５Ａに接触させる（すなわち、気体加圧工程）と同時に薬液２２Ａを排出した。そして、再びクエン酸水溶液（１ｗｔ％）を１０分間循環させて沪過膜モジュール１１Ｂを洗浄し、再び薬液を排出した。すなわち、一種類の薬液を気体加圧工程の前後に２段に組み合わせて洗浄した。その後沪過膜モジュール１１Ｂの純水透過流束を測定したところ、８．０ｍ／日であり、薬洗時間が約２０分間と比較的短い時間で運転前の透過流束の９５％まで回復するという優れた洗浄効果を得ることができた。

【００２５】（実施例３）実施例３においては、実施例１における沪過運転装置１０を用い、定流量沪過運転により透水性能が低下した沪過膜モジュール１１Ｃ（純水透過流束１．６ｍ／日）を、図２に示す薬液洗浄装置２０の沪過膜モジュール２１の代わりに取り付けた。そして開閉弁３２および３９を閉の状態で沪過膜モジュール１１Ｃの透過側から空気圧５０ｋＰａの空気２５Ａを圧入して沪過膜１１Ｒの透過側に１分間空気で接触させた（すなわち、気体加圧工程）後、開閉弁２８、２９、３０、３３、３４、３８および３９を開、開閉弁２７、３１、３２、３５、３６および４０を閉として、ポンプ２４を駆動させ、薬液槽２２中の界面活性剤（ウルトラジル＃５３、ヘンケル白水社製）の１ｗｔ％水溶液を沪過膜モジュール１１Ｃの透過側から圧力１００ｋＰａで１分間圧入透過した。そして、薬液を排出した。その後、沪過膜モジュール１１Ｃの純水透過流束を測定したところ、７．６ｍ／日であり、運転前の透過流束の約９０％まで回復するという優れた洗浄効果を得ることができた。

【００２６】（比較例１）比較例１においては、実施例１における沪過運転装置１０を用い、定流量沪過運転により透水性能が低下した沪過膜モジュール１１Ｄ（純水透過流束１．３ｍ／日）を、図２に示す薬液洗浄装置２０の沪過膜モジュール２１の代わりに取り付けた。そして沪過膜モジュール１１Ｄの透過側に空気を圧入せずに、薬液としてクエン酸水溶液（１ｗｔ％）を実施例１と同様に３０分間循環させて沪過膜モジュール１１Ｄの洗浄を行った後、薬液を排出した。その後、沪過膜モジュール１１Ｄの純水透過流束を測定したところ、５．６ｍ／日であり、薬洗時間を約３０分間要したが、運転前の透過流束の６５％と洗浄回復性は著しく低かった。

【００２７】（比較例２）運転により透水性能が低下した沪過膜モジュール１１Ｅ（純水透過流束１．６ｍ／日）を、図２に示す薬液洗浄装置２０の沪過膜モジュール２１の代わりに取り付けた。そして、沪過膜モジュール１１Ｅの透過側に空気を圧入せずに、実施例３と同様に、薬液槽２２中の界面活性剤（ウルトラジル＃５３、ヘンケル白水社製）の１ｗｔ％水溶液を沪過膜モジュール１１Ｅの透過側から圧力１００ｋＰａで１分間圧入透過して洗浄を行った。そして薬液を排出した。その後、純水透過流束を測定したところ、４．３ｍ／日であり、運転前の透過流束の５１％と洗浄回復性は著しく低かった。

【００２８】

【発明の効果】以上、説明したように、本発明によれば、沪過膜モジュールの薬液洗浄工程に気体加圧工程を適宜に設けることにより、沪過膜モジュールの洗浄効果を著しく向上することができ、薬液の使用量を減らせるとともに、短時間で薬液洗浄が行えることによって、洗浄コストを大幅に下げることができる。

【図面の簡単な説明】

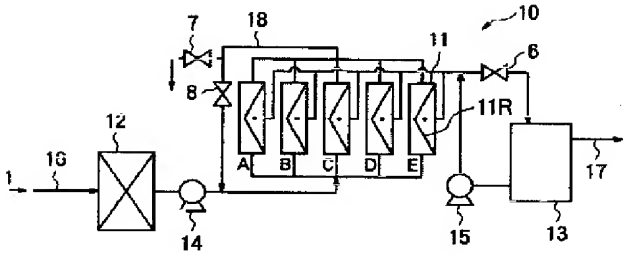
【図１】本発明の沪過膜モジュールの洗浄方法を実施するための沪過膜モジュールを用いた沪過運転装置の概略図

【図２】本発明の沪過膜モジュールの洗浄方法を実施するための沪過膜モジュールの薬液洗浄装置の概略図

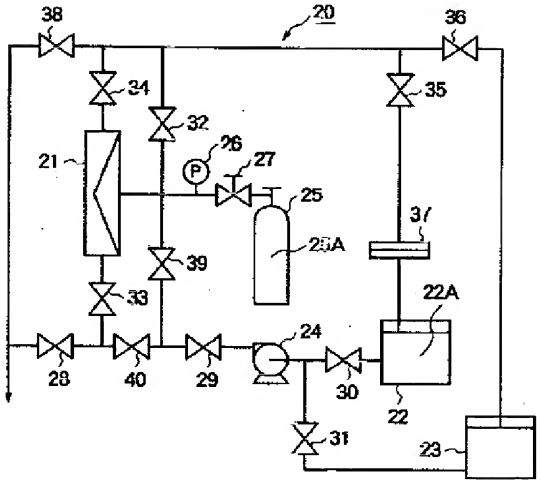
【符号の説明】

１　河川原水、表流水（水）
１０　沪過運転装置（膜浄化システム）
１１　沪過膜モジュール（中空糸膜モジュール）
１１Ｒ　沪過膜（中空糸膜）
２２Ａ　薬液
２５Ａ　空気（気体）

【図１】



【図２】



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METHOD FOR CLEANING FILTER MEMBRANE MODULE
[Rokamaku mojyuhru no senjyoh houhoh]

Nobuyuki Nakatsuka

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INVENTOR	(72):	Nobuyuki Nakatsuka
APPLICANT	(71):	000002901
		Daicel Chemical Co. Ltd.
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Claims

1. A method for cleaning a filter membrane module to restore water permeability by cleaning a filter membrane module degraded in water permeability of the membrane in a purifying system for water by means of a liquid chemical, which method for cleaning a filter membrane module is characterized by the fact that a pressurizing process for pressurizing with a gas is provided from the permeation side of the filter membrane of the filter membrane module at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, under a pressure of at least 20 kPa but below the bubble point for 0.1-5 min.

2. The method for cleaning a filter membrane module described in Claim 1, characterized by the fact that the water used is ground water.

3. The method for cleaning a filter membrane module described in Claim 1 or 2, characterized by the fact that the filter membrane is an ultrafiltration membrane.

4. The method for cleaning of a filter membrane module described in one of Claims 1-3, characterized by the fact that the filter membrane module is a hollow yarn membrane module comprising a hollow yarn membrane.

5. The method for cleaning of a filter membrane module described in one of Claims 1-4, characterized by the fact that the material used for the membrane of the filter membrane is cellulose acetate.

6. The method for cleaning of a filter membrane module described in one of Claims 1-5 characterized by the fact that cleaning with a liquid chemical is done with one type or two or more different types of chemicals selected from among citric acid, a surfactant and sodium hypochlorite in a single step or a multiple-step combination.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a method for cleaning filter membrane modules, and the invention further pertains to a method for cleaning filter membrane modules capable of restoring water permeability in a short cleaning time when cleaning the filter membrane module with a liquid chemical to restore water permeability and cleaning, making safe operation possible for a long time after cleaning.

[0002]

Prior art and problems to be solved by the invention

In the past, as a method for cleaning a filter membrane module with reduced water permeability using a liquid chemical, for example, a method for cleaning a filter membrane module consisting of circulating a liquid chemical upon equalizing the pressure of the permeating liquid and the pressure of the stock solution is disclosed in Japanese Kokai Patent Application No. Sho 61[1986]-11108. Furthermore, a method for cleaning a filter membrane module consisting of injecting a liquid chemical from the permeation side is disclosed in Japanese Kokai Patent Application No. Hei 3[1991]-77629 and Japanese Kokai Patent Application No. Hei 4[1992]-161232, etc. The problem with the methods of the aforementioned cases is that a sufficient cleaning effect cannot be achieved when a cleaning method where a liquid chemical alone is used. When the cleaning effect achieved is insufficient, the amount of liquid chemical used is increased or the cleaning time with the chemical is increased in an attempt to improve the cleaning effect in the aforementioned prior art.

[0003]

Furthermore, a method for cleaning a filter membrane module consisting of injecting a gas from the permeation side is disclosed in, for example, the technical journal, "Membranes" Vol. 20, No. 5, p. 328 (1995). The method disclosed is a back washing method in which the gas injected from the permeation side instantaneously passes through the filter membrane and removes clogging substances to restore the filter flow velocity. However, the injection of gas in this case is not a cleaning method used at the time of a liquid chemical cleaning process, and as a consequence, removal of substances such as iron oxide and manganese oxide adsorbed on the filter membrane is not possible.

[0004]

Based on the above background, the purpose of the present invention is to provide a method for cleaning a filter membrane module capable of sufficiently removing materials adsorbed to the filter membrane, improving efficiency of cleaning, and at the same time, reducing the amount of the liquid chemical used, so that cleaning with a liquid chemical can be done in a short time, and furthermore, the cleaning cost can be decreased in a liquid chemical cleaning process for filter membranes.

[0005]

Means to solve the problem

As a result of much research conducted by the inventors of the present application on feeding of a liquid chemical to the filter membrane module and timing of application of pressure, etc., during the course of the cleaning process with a liquid chemical of a filter membrane module, they found a significant difference in the cleaning effect based on the timing of the pressure applied and the pressure of the gas used, and as a result of further study of types of filter membranes, a combination of the liquid

chemical and the order and number of cleanings with the liquid chemical, etc., the inventors discovered that a superior cleaning effect could be achieved in a short time, and as a result, the present invention was accomplished.

[0006]

Thus, the method for cleaning filter membrane module of the present invention is a method characterized by the fact that a pressurizing process using a gas is provided from the permeation side of the filter membrane of the filter membrane module at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, under a pressure of at least 20 kPa but below the bubble point for 0.1-5 min in a method for cleaning a filter membrane module for restoring water permeability by cleaning a filter membrane module with degraded water permeability in a membrane purifying system for water by means of a liquid chemical.

[0007]

Furthermore, the method for cleaning filter membrane module of the present invention is characterized by the fact that the water used is ground water.

[0008]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the filter membrane is an ultrafiltration membrane.

[0009]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the filter membrane module is a hollow yarn membrane module using a hollow yarn membrane.

[0010]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the material used for the membrane of the filter is a cellulose acetate.

[0011]

And furthermore, the method for cleaning filter membrane module of the present invention is characterized by the fact that the cleaning with a liquid chemical is done with one or two or more different types of chemicals selected from citric acid, a surfactant and sodium hypochlorite in a single step or in a multiple steps.

[0012]

Embodiment of the invention

In the present invention, pressurizing with a gas may be provided at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, and it is desirable when provided either before or before and after the liquid chemical is supplied. In order to physically remove the substances adsorbed on the surface of the filter membrane and to further enhance the cleaning efficiency with the liquid chemical, it is desirable when the aforementioned treatment is done prior to supplying the liquid chemical to the filter membrane module. In the method for cleaning a

filter membrane module of the present invention, the pressure used for introducing of the gas from the permeation side of the filter membrane module is at least 20 kPa but below the bubble point, and at least 40 kPa but below 150 kPa is further desirable. In this case, the reason the pressure of the gas used is specified to be at least a pressure of 20 kPa but below the bubble point is because the cleaning effect is insufficient when the gas pressure used is less than 20 kPa, and the target cleaning recovery cannot be achieved; on the other hand, when the pressure used is at the bubble point or above, the filter membrane module may be physically damaged. In this case, the bubble point varies depending on the material used for the filter membrane, the fraction molecular weight of the filter membrane and the pore diameter of the membrane, and for example, in the case of an acetate cellulose film having a membrane pore diameter of 0.1 μm, a gas pressure of approximately 300 kPa is used.

[0013]

Furthermore, it is not necessary for the gas to permeate the filter membrane and reach the stock solution side at the time of introducing the gas to the permeation side of the membrane in the gas compression process as long as the gas is injected inside the film in the thickness direction from the permeation side of the filter membrane. When injection of the gas is carried out as explained above, the gas enters inside the entire filter membrane in the thickness direction of the filter membrane and the substances clogging the filter membrane are pressed out and uniform cleaning of the interior of the filter membrane module is made possible. When a liquid (liquid chemical) is applied from the permeation side of the filter membrane module as in the case of standard backwashing process, the liquid permeates through regions of the membrane with a lower degree of clogging and permeation through the clogged area is less likely to occur, thus, [complete] cleaning of the clogged regions cannot be achieved and cleaning of the filter membrane becomes non-uniform.

[0014]

In this case, the compression time of the gas (gas compression process) is the duration of time that the gas is applied to the permeation side of the entire filter membrane of the filter membrane module and in general, 0.1-5 min is desirable, and when the cleaning effect and cleaning efficiency are taken into account, 0.5-2 min is desirable. In this case, the reason the compression time of the gas is specified to be in the range of 0.5-5 [sic] min is because the gas cannot sufficiently reach the clogged areas and cleaning efficiency for the clogged area is insufficient when the compression time is .5 min or less; on the other hand, when the compression time is 5 min or longer, an increase in the additional cleaning effect cannot be expected and the cleaning efficiency is reduced.

[0015]

The filter membrane used for the filter membrane module of the present invention is not especially limited, and for example, a microfiltration membrane, ultrafiltration membrane, nanofiltration membrane, reverse osmosis membrane, etc., can be mentioned. When a gas is applied from the permeation side in the microfiltration membrane, permeation of the gas through the filter membrane occurs at times, and as a consequence, uniform cleaning cannot be achieved. Furthermore, in the case of a nanofiltration membrane or reverse osmosis membrane, the pore diameter of the filter membrane is too small and infiltration of the gas into the pores of the filter membrane is insufficient at times; and as a result, uniform cleaning cannot be achieved. For the reasons given above, an ultrafiltration membrane is desirable for the filter membrane of the present invention. In this case, ultrafiltration membrane means a filter membrane having a fraction molecular weight in the range of 10^3-10^6 and a pore diameter in the range of 1-100 nm.

[0016]

As for the film material used for the filter membrane module of the present invention, polymer materials such as polyether sulfone, polyacrylonitrile copolymer and cellulose acetate can be mentioned, and among those listed above, cellulose acetate is especially desirable.

[0017]

As for the form of the membrane of the filter membrane module of the present invention, the plate and frame type, pleated type, spiral type, tubular type (pipe-like type), or hollow yarn type can be mentioned, and among those listed above, the hollow yarn type is especially desirable. Furthermore, when a hollow yarn membrane module is used, the internal pressure system in which the stock solution flows inside the hollow yarn membrane is desirable.

[0018]

As an example of the present invention where cleaning with a liquid chemical is performed with one or two or more different types of chemicals, use of a "combined liquid chemical" consisting of citric acid and a surfactant can be mentioned. Furthermore, the aforementioned single step or a combination of multiple steps with the aforementioned liquid chemical means cleaning once with the aforementioned liquid chemical in a single step or cleaning multiple times with the liquid chemical in multiple steps. As an example of cleaning the filter membrane module using citric acid and a surfactant, many different combinations, for example, (1) an example where cleaning is first performed with citric acid followed by cleaning with a surfactant, (2) cleaning multiple times with a liquid chemical containing both, etc., can be mentioned. Needless to say, the gas pressurizing process may be applied before, during or after

the aforementioned cleanings. The liquid chemical used at the time of the liquid chemical cleaning may be circulated in the untreated water side of the filter membrane or may be circulated from the untreated water side to the permeation side. Furthermore, the liquid chemical may be circulated from the permeation side of the filter membrane to the untreated water side as well.

[0019]

Working examples

The present invention is further explained in detail with working examples and the figures appended below, but the present invention is not limited by these working examples. Figure 1 is a schematic view of a membrane purifying system 10, which is a membrane cleaning system utilized in cleaning filter membrane modules 11A-E in the filter membrane module cleaning system of the present invention, and accessories such as flow meter and pressure gage are omitted in the figure. In Figure 1, 11 is a filter membrane module and consists of a combination of five modules and each is defined as filter membrane module 11A, 11B, 11C, 11D and 11E (represented by 11). In the filter membrane module 11, the material of the membrane used for the filter membrane 11R is a cellulose acetate, and represents a hollow yarn membrane module comprising a hollow yarn, and each hollow yarn membrane comprises a hollow yarn having an inner diameter of 0.8 mm and an outer diameter of 1.3 mm, and the membrane area of a single module is 0.5 m^2. Furthermore, 12 is a pre-filter, and the pre-filter is used for removal of impurities included in the ground water, which is the water supplied to the filter membrane module 11. Furthermore, 13 is a permeated water tank, and the permeated water tank is used for temporary storage of the permeated water from the filter membrane module 11. Furthermore, 14 and 15 are pumps, and 6, 7 and 8 are two-way valves.

[0020]

In this case, two-way valve 7 is closed and two-way valves 6 and 8 are opened at the time of filtration treatment. The raw river water 1 used as the ground water is supplied from the water supply pipe 16, impurities are removed by the pre-filter 12 and the aforementioned ground water is supplied to five filter membrane modules 11A-11E by pump 14. In the filter membrane module 11, the raw river water is supplied to the hollow core of the hollow yarn membrane 11R, and the permeated water filtered by internal pressure cross flow filtration passes through the two-way valve 6 and is collected, temporarily stored in the permeated water tank 13 and is delivered from the pipe 17 as a purified water. The unfiltered untreated water passes through the two-way valve 8 through the circulating pipe 18 and is recycled. The filter of the filter membrane module 11 is a steady flow filtration at a set filtration flow velocity of 1.5 m/day at a cross flow line speed of 0.2 m/s. Furthermore, a back washing process consisting of supplying the permeated water from the permeation side of the filter membrane module for 1 min at a ratio of once every 45 min is provided and the water recovery percentage is 90%. During the course of the back wash operation, the two-way valve 7 is opened and the two-way valves 6 and 8 are closed and pump 14 is stopped. Furthermore, a back wash operation consisting of supplying a portion of the permeated water to the permeation side of the filter membrane module 11 through pump 15, which is the reverse of the normal operation, is periodically provided.

[0021]

Working Example 1

Figure 2 illustrates Working Example 1 of the present invention, and 20 is a membrane purifying system for filter membrane module used in the method for cleaning filter membrane module of the present invention. First, the structure of the membrane purification system 20 shown in Figure 2 is

explained. In this case, 21 is a filter membrane module, 22 is a liquid chemical tank for storing the liquid chemical 22A used for cleaning the filter membrane module, 23 is a pure water tank containing purified water, 24 is a pump, 25 is an pneumatic tank containing compressed air 25A used as a gas, 26 is a pressure gage, 27 is a pressure regulating valve, 28, 29, 30, 31, 32, 33, 34, 35, 36, 38, 39 and 40 are two-way valves and 37 is a filter. In the aforementioned membrane purification system 20, the valve of the pneumatic tank 25 is opened while the two-way valves 32 and 39 are closed and the pressure regulating valve 27 is adjusted so that the compressed air 25A can be injected into the permeation side of the filter membrane module 21 at a specific pressure. Furthermore, when pump 24 is turned on while two-way valves 29, 30, 33, 34, 35 and 40 are open and two-way valves 28, 31, 32, 36, 38 and 39 are closed, it is possible to circulate the liquid chemical 22A inside the liquid chemical tank 22 and to clean the filter membrane module 21 with the liquid chemical. After the cleaning is completed, the two-way valve 28 is opened to release liquid chemical 22A, then, two-way valves 31, 29, 33, 34, 36, 32 and 40 are opened and two-way valves 30, 28, 35, 38 and 39 are closed and the pump is turned on and the purified water permeation flow is measured to obtain the recovery ratio.

[0022]

In the aforementioned working example, first, five filter membrane modules 11A-E having a purified water permeation capacity with a purified water permeation flow rate of 8.4 m/day were mounted in the filter membrane module 11 in the membrane purification system 10 shown in Figure 1. Furthermore, untreated river water (ground water) 1 obtained from a river was supplied from water supply pipe 16, and filtration treatment was initiated. The filtration treatment in this case is an internal pressure cross flow filtration (cross flow line speed 0.2 m/s) in which the untreated water is supplied to the interior of the hollow yarn membrane and a steady flow filtration at a set filtration flow rate of 1.5 m/day was used.

In this case, a back wash process consisting of flowing the permeated water from the permeation side of the filter membrane module for 1 min was provided every 45 min during the operation to achieve a water recovery percentage of 90%. In the aforementioned filtration treatment under the steady flow filtration treatment, the filter membrane was contaminated with impurities included in the untreated water and the filter pressure slowly increased as a result of clogging, and the filter pressure reached 10 kPa in all of five filter membrane modules approximately 8 months after the start of the treatment and continued treatment was not possible. When the aforementioned five filter membrane modules 11A-11E were removed from the membrane purification system 10 and were replaced with the filter membrane module 21 of the membrane purification system 20 shown in Figure 2, and when purified water was filtered through the filter membrane module 11 under an air pressure of 100 kPa and the purified water permeation flow rate was measured, a value of 1.3-1.8 m/day was achieved in all cases and a significant reduction in the permeation performance from that of the initial purified water permeation flow rate of 8.4 m/day was observed.

[0023]

After the aforementioned treatment, cleaning was of the filter membrane module 11 was conducted. First, the filter membrane module 21 of the membrane purification system 20 was replaced with the filter membrane module 11A used for the aforementioned treatment (purified water permeation flow rate of 1.5 m/day), the air 25A with the air pressure adjusted to 50 kPa by the pressure regulating valve 27 was injected into the permeation side of the filter membrane module 21 from the pneumatic tank 25 for 1 min while the two-way valves 32 and 39 were closed. That is, a gas compression process was provided. Furthermore, in order to perform the liquid chemical cleaning, two-way valves 29, 30, 33, 34, 35 and 40 were opened and two-way valves 28, 31, 32, 36, 38 and 39 were closed, and pump 24 was turned on,

and furthermore, an aqueous solution of citric acid (1 wt%) inside the liquid chemical tank was circulated for 30 min under the mean line speed on the membrane surface of 0.5 m/s and cleaning was performed for the aforementioned filter membrane module with a liquid chemical; then, the two-way valve 28 was opened and the aforementioned liquid chemical was released. Subsequently, when the purified water permeation flow rate of the filter membrane module 11A was measured according to the procedure described above, a flow rate of 8.3 m/day was achieved, and an excellent cleaning efficiency, that is, an excellent recovery factor that was essentially the same as the permeation flow rate before the treatment was achieved.

[0024]

Working Example 2

In Working Example 2, the membrane purification system 10 described in Working Example 1 was used and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11B (purified water permeation flow rate of 1.8 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. Furthermore, before injecting air to the permeation side of the filter membrane module 11B, an aqueous solution of citric acid (1 wt%) was circulated for 10 min to clean the membrane; then, compressed air 25A at an air pressure of 100 kPa was injected into the permeation side to bring the permeation side of the filter membrane module 11B so that it came in contact with air 25A for 1 min and at the same time, the liquid chemical 22A was released (that is, gas compression process). Furthermore, the aqueous solution of citric acid (1 wt%) was circulated for 10 min to clean the filter membrane module 11B and the liquid chemical was released for a second time. In other words, cleaning was performed with one type of liquid chemical in two steps, one before and one after the gas compression process. When the purified water

permeation flow rate of the filter membrane module 11B was measured, a rate of 8.0 m/day was obtained, and an excellent cleaning efficiency, that is, excellent restoration of the permeation flow rate to 95% of the value prior to treatment was achieved in a relatively short cleaning time of approximately 20 min with a liquid chemical.

[0025]

Working Example 3

In Working Example 3, the membrane purification system 10 described in Working Example 1 was used, and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with filter membrane module 11C (purified water permeation flow rate 1.6 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. Furthermore, compressed air 25A with an air pressure of 50 kPa was injected from the permeation side of the filter membrane module 11C while the two-way valve 32 was opened and 39 was closed and brought into contact with the permeation side of the filter membrane module 11R for one minute (that is, gas compression process); then, the pump 24 was turned on while the two-way valves 28, 29, 30, 33, 34, 38 and 39 were opened and the two-way valves 27, 31, 32, 35, 36 and 40 were closed, and furthermore, a 1 wt% aqueous solution of a surfactant (Ultrasil #53, [transliteration] Product of Henchel Hakusui Co.) included in the liquid chemical tank 22 was injected from the permeation side of the filter membrane module 11C under a pressure of 100 kPa for 1 min. And finally, the liquid chemical was released. Furthermore, when measurements were made for the purified water permeation flow rate of the filter membrane module 11C, a rate of 7.6 m/day was obtained, and excellent cleaning efficiency, that is, restoration of the permeation flow rate to 90% of the value prior to [water] treatment was achieved in this case as well.

[0026]

Comparative Example 1

In Comparative Example 1, the membrane purification system 10 described in Working Example 1 was used and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11D (purified water permeation flow rate 1.3 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. In this case, injection of compressed air to the permeation side of the filter membrane module 11D was omitted and an aqueous solution of citric acid (1 wt%) was circulated for 30 min as in the case of Working Example 1 and cleaning the filter membrane module 11D was performed, and the liquid chemical was subsequently released. Subsequently, when the purified water permeation flow rate of the filter membrane module 11D was measured, a rate of 5.6 m/day was achieved and the cleaning recovery factor measured was significantly lower and was only 65% of the permeation flow rate before [water] treatment even though approximately 30 min of the cleaning time was provided.

[0027]

Comparative Example 2

The filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11E (purified water permeation flow rate of the filter membrane module 11D, 1.6 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. In this case, injection of compressed air to the permeation side of the filter membrane module 11E was omitted and a 1 wt% aqueous solution of a surfactant (Ultrasil #53, [transliteration] Product of Henchel Hakusui Co.) was injected from the permeation side of the filter

membrane module 11E under a pressure of 100 kPa according to the procedure described in Working Example 3 and cleaning was performed. Subsequently, the liquid chemical was released. When measurements were made, a rate of 4.3 m/day was achieved and the cleaning recovery factor was significantly lower at 51% of the permeation flow rate before [water] treatment.

[0028]

Effect of the invention

As explained in detail above, according to the present invention, a significant improvement in the cleaning efficiency of the filter membrane module can be achieved when a gas compression process is appropriately provided during a liquid chemical cleaning process, furthermore, a reduction in the amount of liquid chemical required is made possible, and furthermore, cleaning with a liquid chemical in a short time is possible, resulting in a significant reduction in the cleaning cost.

Brief description of the figures

Figure 1 is a schematic view of a membrane purification system utilizing a filter membrane module used in application of the method for cleaning a filter membrane module of the present invention.

Figure 2 is a schematic view of a liquid chemical cleaning device for filter membrane modules used for applying the method for cleaning filter membrane modules of the present invention.

Explanation of symbols

1 Untreated river water, surface water (water)

10 Membrane purification system (membrane cleaning system)

11 Filter membrane module (hollow yarn membrane module)

11R Filter membrane (hollow yarn membrane)

22A Liquid chemical

25A Air (gas)

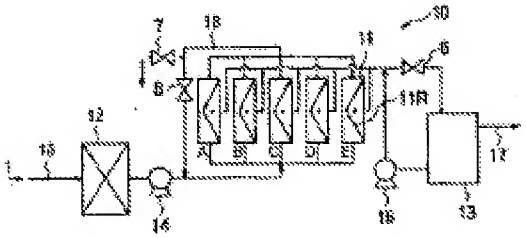

Figure 1

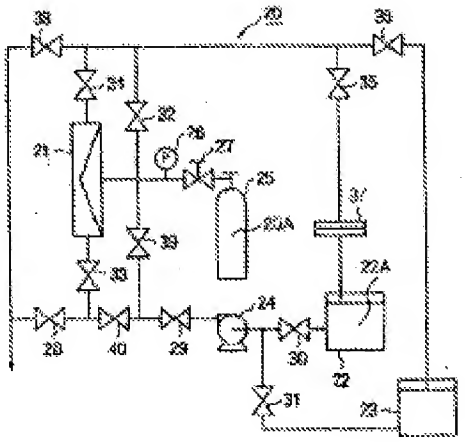

Figure 2